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(71) Applicant: **EASTMAN KODAK COMPANY**  
**343 State Street**  
**Rochester New York 14650-2201(US)**

(72) Inventor: **Miller, Gary Roger, c/o Eastman**  
**Kodak Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201(US)**  
Inventor: **Walls, John E., c/o Eastman Kodak**  
**Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201(US)**  
Inventor: **Felker, Melanie Ann, c/o Eastman**  
**Kodak Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201(US)**

(74) Representative: **Nunney, Ronald Frederick**  
**Adolphe et al**  
**Kodak Limited**  
**Patent Department**  
**Headstone Drive**  
**Harrow Middlesex HA1 4TY (GB)**

(54) **Aqueous developer for lithographic printing plates which exhibits reduced sludge formation.**

(57) Aqueous alkaline developing compositions useful in the development of negative-working lithographic printing plates are comprised of an organic solvent, an anionic surface active agent, an alkali metal tetraborate, an alkali metal salt of an aliphatic monocarboxylic acid, an alkali metal salt of an aliphatic dicarboxylic acid, an alkali metal citrate, a poly(alkylene glycol), an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid and sufficient alkaline buffering system to provide an alkaline pH. The developing composition is resistant to oxidation, highly effective in dissolution-type processing, able to effectively desensitize the background areas of the printing plate, and capable of preventing excessive deposits in a processing machine and rapidly redissolving deposits that do form.

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## FIELD OF THE INVENTION

This invention relates in general to lithography and in particular to a developing composition for developing lithographic printing plates and similar photographic elements. More specifically, this invention relates to a novel aqueous developer for removing the non-image area of negative-working lithographic printing plates.

## BACKGROUND OF THE INVENTION

The art of lithographic printing is based upon the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and the water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water and repels the ink while the image area accepts the ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced; such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

The most common type of lithographic printing plate to which the present invention is directed has a light-sensitive coating applied to an aluminum base support. The coating may respond to light by having the portion which is exposed become soluble so that it is removed in the developing process. Such a plate is referred to as positive-working. Conversely, when that portion of the coating which is exposed becomes hardened the plate is referred to as negative-working. In both instances the image area remaining is ink-receptive or oleophilic and the non-image area or background is water-receptive or hydrophilic. The differentiation between image and non-image areas is made in the exposure process where a film is applied to the plate with a vacuum to insure good contact. The plate is then exposed to a light source, a portion of which is composed of UV radiation. In the instance where a positive plate is used, the area on the film that corresponds to the image on the plate is opaque so that no light will strike the plate, whereas the area on the film that corresponds to the non-image area is clear and permits the transmission of light to the coating which then becomes more soluble and is removed. In the case of a negative plate the converse is true. The area on the film corresponding to the image area is clear while the non-image area is opaque. The coating under the clear area of film is hardened by the action of light while the area not struck by light is removed. The light-hardened surface of a negative plate is therefore oleophilic and will accept ink while the non-image area which has had the coating removed through the action of a developer is desensitized and is therefore hydrophilic.

The present invention provides a novel aqueous developer for negative-working lithographic printing plates. Most developer compositions for negative-working printing plates disadvantageously consist primarily of organic solvents which are offensive through their volatility and high concentration, pose toxic exposure hazards to the end user and are pollutants to the environment when evaporated into the air and/or discharged into public waterways. Presently there is a trend toward the use of aqueous developers. Typically, these aqueous developers also contain organic solvents at concentrations which are still environmentally harmful and toxic to the end user. The prime advantage is that the solvents are not odor-wise offensive. They have the disadvantage of having a strongly alkaline pH, cause redeposit on the plate and machine parts, and solubilize the coating residue which creates disposal problems and reduces the effective life of the developer in a processing machine. The present invention provides a composition which substantially alleviates these problems.

Aqueous alkaline developing compositions, for use with negative-working lithographic printing plates, which contain an organic solvent and a surface active agent are well known. Such developing compositions are described for example in U.S. Patents 3,701,657, 3,707,373, 4,186,006, 4,308,340, 4,350,756, 4,395,480, 4,716,098, 5,035,982, European Patent No. 0 080 042, British Patent No. 1,515,174 and British Patent No. 2,110,401. As disclosed in U.S. Patents 3,701,657, 3,707,373, 4,350,756, 4,395,480 and 4,716,098 it is also known to incorporate in such developing compositions an aliphatic carboxylic acid or salt thereof. Such developers are generally quite effective but suffer from disadvantages which have hindered their commercial utilization, for example, they may not be able to adequately desensitize residual coating which remains in the background areas of the printing plate.

One of the more serious problems which can afflict negative-working lithographic printing plates is inability of the developer to remove all residual coating from the non-image areas of the plate. When sufficient residual coating remains, a condition exists for background sensitivity to occur during the printing process. Minimally, the effect would be to increase the amount of water required in the fountain solution.

Under more severe conditions, ink may adhere to the background and ultimately to the printed sheet, thereby resulting in a condition known as "tinting" or "toning." Under extremely severe conditions, there is so much ink in the background that it is referred to as "scumming."

Among the requirements for an effective developer are (1) that it be resistant to oxidation, (2) that it be capable of dissolution-type processing, i.e., that the photosensitive composition dissolves fully in the developing solution rather than breaking up in the form of particles, and (3) that it be effective in desensitizing the non-image areas.

A particularly advantageous negative-working lithographic printing plate comprises an imaging layer containing a diazo resin, an acid-substituted ternary acetal polymer and an unsaturated polyester. One of its major advantages is its ability to resist blinding. As is well understood in the art, the term "blinding" refers to inability of the image areas to adequately take up the printing ink. In this printing plate, an important feature contributing to the ability to resist blinding is the presence of the unsaturated polyester. However, these plates sometimes exhibit a yellow stain. The use of the unsaturated polyester is, in part, connected with the stain. There appear to be other, as yet poorly understood, factors contributing to the stain. The yellow stain is known to be an extremely thin but strongly adhering layer of diazo resin and polymeric binder which is not removed in the developing process when conventional developers are used. The intensity of the stain is proportional to the amount of residual coating.

In general, a developer that slowly penetrates and slowly releases the coating from the non-image areas of the printing plate is satisfactory for use in hand processing. The platemaker can continue the development step until the plate is visually clean. However, in machine processing the plate has a defined dwell time in the developer section of the machine and the coating must be completely removed during this operation or background sensitivity can occur. Slow processing in the machine also increases the likelihood of contaminating the brushes (or pluses) and rollers in the machine, thus increasing the chance of coating redepositing back onto the plate from these contaminated surfaces. Machine developers function best when they penetrate and release the coating quickly from the non-image areas of the plate.

Another serious problem in this art is the inability of the developer to resolubilize materials that do dry on the surfaces, rollers, and brushes of machine processors. If dissolved coating adheres to the interior panels, brushes (or pluses) or rollers of the machine, either during the processing operation or during an idle period, it is important that the developer rapidly redissolve these materials before they can transfer to the non-image areas of the plate and cause background sensitivity.

It is toward the objective of providing a new and improved aqueous developer, for use with negative-working lithographic printing plates, which has more rapid developing action and which prevents excessive deposits in the processing machine, or rapidly redissolves deposits that have formed, that the present invention is directed.

### SUMMARY OF THE INVENTION

In accordance with this invention, an aqueous alkaline developing composition which is useful in the development of negative-working lithographic printing plates is comprised of:

- (1) an organic solvent,
- (2) an anionic surface active agent,
- (3) an alkali metal tetraborate,
- (4) an alkali metal salt of an aliphatic monocarboxylic acid, preferably containing 6 to 22 carbon atoms,
- (5) an alkali metal salt of an aliphatic dicarboxylic acid, preferably containing 4 to 16 carbon atoms,
- (6) an alkali metal citrate,
- (7) a poly(alkylene glycol)
- (8) an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid, and
- (9) an alkaline buffering system in an amount sufficient to provide an alkaline pH.

The aqueous developer of this invention contains ingredients which have been unexpectedly found to function in combination to promote developing action, prevent excessive sludge formation and enhance the ability of the developer to rapidly redissolve deposits. These ingredients, as described hereinafter in greater detail, are an alkali metal citrate, a poly(alkylene glycol) and an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid.

The aqueous developer of this invention can be employed in the development of any of a wide variety of negative-working lithographic printing plates. Thus, for example, it can be employed with lithographic printing plates containing the acetal polymer binders described in any of U.S. Patents 4,652,604, 4,741,985 and 4,940,646. It can be employed with printing plates containing binary acetal polymers as described in U.S. Patent No. 5,169,897, issued December 8, 1992. It can be employed with printing plates containing

acid-substituted ternary acetal polymers as described in U.S. Patent No. 5,169,898, issued December 8, 1992. It is especially advantageous for use with lithographic printing plates comprising both an acid-substituted ternary acetal polymer and an unsaturated polyester.

The aqueous developer of this invention has many advantageous features. Thus, for example, it requires only a low concentration of organic solvent yet is highly effective in dissolution-type processing. It is highly resistant to oxidation. Most significantly, it is very effective in overcoming the problems of excessive background sensitivity and at the same time is capable of providing reduced sludge formation, faster processing and a cleaner processing machine. It is capable of providing a long processing cycle (>15 square meters per liter of developing solution) with essentially no change in the quality of processing, while at the same time offering complete removal of yellow stain on even the most severely stained plates.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

As indicated hereinabove, the ingredients required in the aqueous alkaline developing composition of this invention are (1) an organic solvent, (2) an anionic surface active agent, (3) an alkali metal tetraborate, (4) an alkali metal salt of an aliphatic monocarboxylic acid, preferably containing 6 to 22 carbon atoms, (5) an alkali metal salt of an aliphatic dicarboxylic acid, preferably containing 4 to 16 carbon atoms, (6) an alkali metal citrate, (7) a poly(alkylene glycol), (8) an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid, and (9) an alkaline buffering system in an amount sufficient to provide an alkaline pH.

The function of the organic solvent is to assist in the removal of the non-exposed portions of the photosensitive coating. Any of a wide variety of solvents can be used, with those typically employed being high boiling liquids. The most preferred solvent is 2-phenoxy propanol due to its excellent solvent action and very low toxicity. Other suitable solvents include, but are not restricted to, 2-phenoxy ethanol, benzyl alcohol, N-methyl pyrrolidone, butyrolactone, propylene glycol monomethyl ether and the like. The organic solvent can be employed in the developing composition in an amount of from about 0.2 to about 16 weight percent, more preferably in an amount of from about 1 to about 10 weight percent, and most preferably in an amount of from about 2.5 to about 7 weight percent.

The anionic surface active agent serves to reduce the surface tension so as to facilitate better penetration of the developer into the coating as well as to provide some cleaning action and dispersion of the coating composition that is removed. Any of a wide variety of anionic surface active agents, especially sulfate and sulfonate alkyl and aryl alkyl anionic surface active agents, can be used. Sodium octyl sulfate is preferred. Other suitable anionic surface active agents include, but are not restricted to, potassium decyl sulfate, sodium toluene sulfonate, sodium xylene sulfonate, sodium dodecylbenzene sulfonate, potassium tridecylbenzene sulfonate, lithium dinonadecylbenzene sulfonate, sodium docosanylbenzene sulfonate, potassium methyl naphthalene sulfonate, lithium triethyl naphthalene sulfonate, sodium isopropyl naphthalene sulfonate, sodium diisopropyl naphthalene sulfonate, sodium dibutyl naphthalene sulfonate, and the like. The anionic surface active agent can be employed in the developing composition in an amount of from about 0.2 to about 15 weight percent, more preferably in an amount of about 0.8 to about 12 weight percent and most preferably in an amount of about 1.2 to about 8 weight percent.

The alkali metal tetraborate serves to elevate the activity of the developing composition, particularly as it relates to the desensitization of the background. Potassium tetraborate is preferred for this purpose but sodium tetraborate and lithium tetraborate are also useful. The alkali metal tetraborate can be employed in the developing composition in an amount of from about 0.01 to about 7 weight percent, more preferably in an amount of about 0.05 to about 5 weight percent, and most preferably in an amount of from about 0.1 to about 3 weight percent.

The function of the alkali metal salt of an aliphatic monocarboxylic acid is to effectively remove diazo resin from the background areas as well as partially insolubilized diazo resin from and around the image area, thereby precluding or at least minimizing the possibility of "hot-spot" formation or halation. Preferred aliphatic monocarboxylic acids for this purpose are those containing 6 to 22 carbon atoms. The most preferred aliphatic monocarboxylic acid is nonanoic acid (also known as pelargonic acid). Other suitable aliphatic monocarboxylic acids include, but are not restricted to, hexanoic acid, octanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, pentadecanoic acid, octadecanoic acid, eicosanoic acid, docosanoic acid, and the like. The alkali metal salt of an aliphatic monocarboxylic acid can be employed in the developing composition in an amount of from about 0.5 to about 12 weight percent, more preferably in an amount of about 1.5 to about 10 weight percent, and most preferably in an amount of about 2.5 to about 8 weight percent.

The function of the alkali metal salt of an aliphatic dicarboxylic acid is to enhance the desensitization of both image and background areas. When salts of both an aliphatic monocarboxylic acid and an aliphatic

dicarboxylic acid are incorporated in the developer, the degree to which the background is cleaned is significantly and surprisingly improved in comparison with use of only a salt of an aliphatic monocarboxylic acid or only a salt of an aliphatic dicarboxylic acid. Preferred aliphatic dicarboxylic acids for this purpose are those containing 4 to 16 carbon atoms. The most preferred aliphatic dicarboxylic acid is sebacic acid.

Other suitable aliphatic dicarboxylic acids include, but are not restricted to, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, dodecanedioic acid, hexadecanedioic acid, and the like. The alkali metal salt of an aliphatic dicarboxylic acid can be employed in the developing composition in an amount of from about 0.05 to about 10 weight percent, more preferably in an amount of about 0.2 to about 5 weight percent, and most preferably in an amount of about 0.4 to about 3 weight percent.

In the developing composition of this invention, the alkali metal citrate, the poly(alkylene glycol) and the alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid function together to effectively reduce sludge formation and provide other beneficial characteristics.

Useful alkali metal citrates for the purpose of this invention include sodium, potassium and lithium salts of citric acid such as, for example, trisodium citrate, tripotassium citrate and trilithium citrate. The alkali metal citrate can be used in an amount of from about 0.1 to about 5 weight percent, more preferably in an amount of about 0.3 to about 4 weight percent, and most preferably in an amount of about 0.4 to about 2 weight percent.

Useful poly(alkylene glycols) for the purpose of this invention include those comprising ethyleneoxy, propyleneoxy or butyleneoxy groups and having a molecular weight in the range of from about 200 to about 2000. The poly(ethylene glycols) are preferred. Especially useful poly(ethylene glycols) include those sold by UNION CARBIDE CORPORATION under the trademarks CARBOWAX 200, CARBOWAX 350 and CARBOWAX 600. The poly(alkylene glycol) can be used in an amount of from about 0.1 to about 5 weight percent, more preferably in an amount of about 0.3 to about 4 weight percent, and most preferably in an amount of about 0.4 to about 2 weight percent.

Both alkali metal salts of an hydroxylated aromatic carboxylic acid and alkali metal salts of an hydroxylated aromatic sulfonic acid are useful for the purpose of this invention. Examples of hydroxylated aromatic carboxylic acids include p-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3-hydroxy-2-naphthoic acid and the like. Examples of hydroxylated aromatic sulfonic acids include hydroquinone sulfonic acid and 4,5-dihydroxy-1,3-benzenedisulfonic acid. The alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid can be used in an amount of from about 0.1 to about 5 weight percent, more preferably in an amount of about 0.3 to about 4 weight percent, and most preferably in an amount of about 0.4 to about 2 weight percent.

Since the developing composition must be alkaline, salts of the acids are employed to formulate the developing composition or are formed in its manufacture. Potassium hydroxide is preferably used to form the potassium salts although sodium and lithium salts are also useful. Potassium carbonate is advantageously employed to provide the desired working pH and to impart buffering capability, but other common buffering agents, such as, for example, trisodium phosphate, disodium phosphate, sodium phthalate, sodium citrate, sodium ascorbate, and sodium tartrate, can be used if desired.

The alkaline buffering system, for example, the combination of potassium hydroxide and potassium carbonate, can be utilized in any amount sufficient to provide an alkaline pH. The pH of the working strength developing composition is preferably in the range of from 8 to 12, more preferably in the range of 8.5 to 11, and most preferably in the range of 9 to 10. Suitable amounts of potassium hydroxide or other alkaline salt-forming agents are in the range of from about 0.1 to about 8 weight percent, more preferably in the range of about 0.05 to about 6 weight percent, and most preferably in the range of about 0.1 to about 3 weight percent. The potassium hydroxide or other alkaline agent, is preferably used only in the mole ratio required to form salts of the carboxylic acids or in just a slight excess over this amount.

In addition to the required ingredients specified above, various optional ingredients can also be included in the developing composition. Examples of such optional ingredients include sodium oxalate and sodium nitrate which are useful as desensitizers. Another useful optional ingredient is an antifoaming agent and particularly useful antifoaming agents are polydimethyl siloxanes such as BURST RSD-10 Antifoam which is commercially available from HYDROLABS Company, Wayne, New Jersey. The antifoam is preferably used in the developing composition in an amount in the range from about 0.001 to about 3 weight percent, more preferably in the range from about 0.005 to about 1 weight percent, and most preferably in the range of from about 0.01 to about 0.5 weight percent.

In a preferred embodiment of the invention, the developing composition comprises:

- (1) an organic solvent,
- (2) an anionic surface active agent,
- (3) an alkali metal tetraborate,

- (4) an alkali metal salt of an aliphatic monocarboxylic acid, preferably containing 6 to 22 carbon atoms,
- (5) an alkali metal salt of an aliphatic dicarboxylic acid, preferably containing 4 to 16 carbon atoms,
- (6) an alkali metal citrate,
- (7) a poly(alkylene glycol),
- (8) an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid,
- (9) a long chain aliphatic amine, and
- (10) an alkaline buffering system in an amount sufficient to provide an alkaline pH.

The incorporation of a long chain aliphatic amine in a developing composition for use with negative-working lithographic printing plates is especially useful in providing enhanced oleophilicity to the image areas of the plate and in providing improved removal of coating residuals. The term "a long chain aliphatic amine" is employed to mean an aliphatic amine having at least one alkyl group containing at least six carbon atoms attached to the amino nitrogen atom.

The long chain aliphatic amine is employed in the developing composition in an amount of from about 0.05 to about 5 weight percent, more preferably in an amount of about 0.1 to about 2 weight percent, and most preferably in an amount of about 0.2 to about 0.8 weight percent. Useful long chain aliphatic amines include primary, secondary and tertiary aliphatic amines. Specific examples of such amines include:

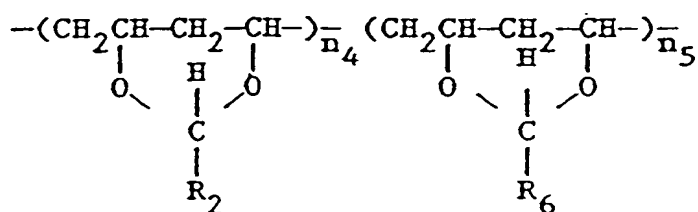
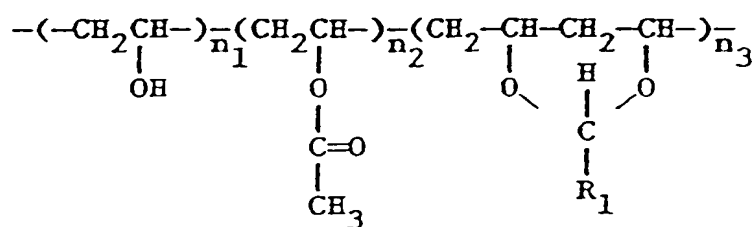
- n-hexyl amine
- n-octyl amine
- n-decyl amine
- n-dodecyl amine
- n-hexadecyl amine
- n-octadecyl amine
- di-n-octyl amine
- tri-n-octyl amine
- N-ethyl-di-hexyl amine
- N-methyl-dioctyl amine
- N-propyl-dioctyl amine
- and the like.

As described hereinabove, the aqueous alkaline developing composition of this invention is especially well adapted for use with lithographic printing plates comprised of a support having thereon a radiation-sensitive layer comprising a diazo resin, an acid-substituted ternary acetal polymer, and an unsaturated polyester.

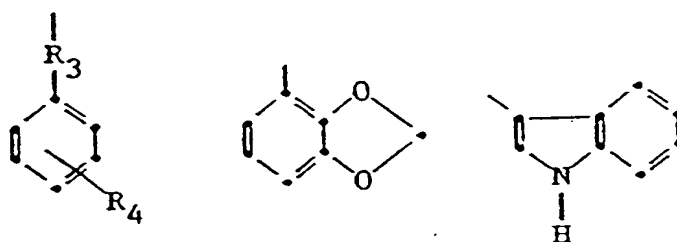
The useful diazo resins include, for example, the condensation product of p-diazo diphenyl amine and paraformaldehyde, the condensation product of 3-methoxy-4-diazo diphenylamine and paraformaldehyde, and the diazo resins of U. S. patents 2,063,631, 2,667,415, 2,667,498, 2,922,715, 2,946,683, 3,050,502, 3,163,633, 3,227,074, 3,311,605, 3,406,159, 3,679,419, 3,849,392 and 3,867,147.

The diazo resin is typically employed in an amount of about 20 to about 70 percent by weight of the photosensitive layer, more preferably in an amount of about 30 to about 60 percent by weight, and most preferably in an amount of about 40 to about 55 percent by weight. The acid-substituted ternary acetal polymer is typically employed in an amount of about 20 to about 75 percent by weight of the photosensitive layer, more preferably in an amount of about 30 to about 60 percent by weight, and most preferably in an amount of about 35 to about 50 percent by weight. The unsaturated polyester is typically employed in an amount of from about 5 to about 40 percent by weight of the photosensitive layer, more preferably in an amount of about 8 to about 30 percent by weight, and most preferably in an amount of about 10 to about 20 percent by weight.

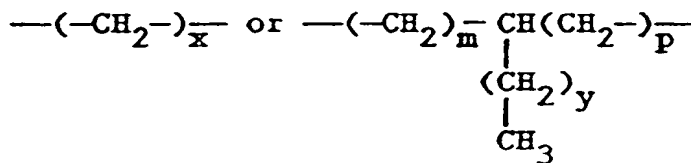
The acid-substituted ternary acetal polymers have recurring units represented by the formula:



wherein  $R_1$  is  $-\text{H}$ ,  $-\text{C}_n\text{H}_{2n+1}$  or  $-\text{C}_n\text{H}_{2n}\text{OH}$  where  $n = 1-12$   
 $R_2$  is



where  $R_3$  is



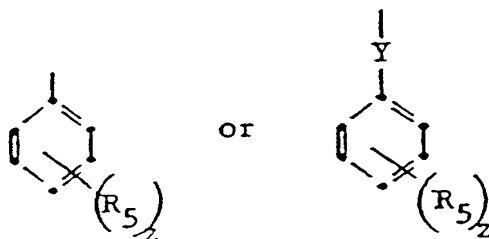
and  $x = 0-8$

$m = 0-8$

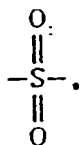
$y = 0-8$

$p = 0-8$

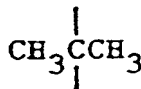
$R_4 = -\text{H}$ ,  $-\text{R}_5$ ,



in which Y = -O-, -S-,



-CH<sub>2</sub>-, -NH- or



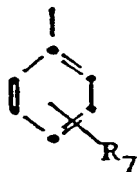
R<sub>5</sub> = -OH, -CH<sub>2</sub>OH, -OCH<sub>3</sub>, -COOH or -SO<sub>3</sub>H

z = 1 to 3

R<sub>6</sub> = -(CH<sub>2</sub>)<sub>a</sub>-COOH

-(CH<sub>2</sub>)<sub>a</sub>-COO<sup>⊖</sup>M<sup>⊕</sup>

or



where

R<sub>7</sub> = -COOH, -COO<sup>⊖</sup>M<sup>⊕</sup>, -(CH<sub>2</sub>)<sub>a</sub>COOH, -O-(CH<sub>2</sub>)<sub>a</sub>COOH,

-SO<sub>3</sub>H, -SO<sub>3</sub><sup>⊖</sup>M<sup>⊕</sup>, -PO<sub>3</sub>H<sub>2</sub>, -PO<sub>3</sub><sup>⊖</sup>M<sub>2</sub><sup>⊕</sup>

-PO<sub>4</sub>H<sub>2</sub> or -PO<sub>4</sub><sup>⊖</sup>M<sub>2</sub><sup>⊕</sup>,

a = 0 to 8

M = Na, K, Li or NH<sub>4</sub>

and n<sub>1</sub> = 0-25 mole %, preferably 3 to 15 mole %

n<sub>2</sub> = 2-25 mole %, preferably 5 to 15 mole %

n<sub>3</sub> = 10-70 mole %, preferably 15 to 50 mole %

n<sub>4</sub> = 10-60 mole %, preferably 12 to 45 mole %

n<sub>5</sub> = 10-45 mole %, preferably 15 to 30 mole %

As indicated by the above structural formula, the acid-substituted ternary acetal polymers can be tetramers, in which the recurring unit comprises a vinyl acetate moiety and first, second and third cyclic acetal groups, or pentamers in which the recurring unit comprises a vinyl alcohol moiety, a vinyl acetate moiety and first, second, and third cyclic acetal groups.



All three of the acetal groups are six-membered cyclic acetal groups, one of them is unsubstituted or substituted with an alkyl or hydroxyalkyl group, another is substituted with an aromatic or heterocyclic moiety, and a third is substituted with an acid group, an acid-substituted alkyl group or an acid-substituted aryl group.

5 The acid-substituted ternary acetal polymers can be prepared by hydrolyzing polyvinyl acetate, or by starting with partially hydrolyzed polyvinyl acetate, i.e. polyvinyl alcohol, and reacting it with three different aldehydes to thereby form a ternary acetal. Suitable techniques for forming polymers of this type are known to those skilled in the art. Thus, for example, the ternary acetal polymers can be prepared by an emulsion  
10 condensation wherein, as the solubility of the starting material changes from water-soluble to solvent-soluble as a result of the formation of the acetal groups, the product forms an emulsion because of its lack of solubility in water. In this method, the particles are prevented from aggregating by use of a surfactant.

An alternative method is to compensate for the change in solubility of the starting material from water-soluble to solvent-soluble by maintaining a homogeneous solution through the continual addition of an appropriate solvent. In the former process, the precipitated particles are filtered, washed and dried. In the  
15 latter process, the reaction solution is added to water and mixed in a blender or homogenizer to precipitate the resin product and create particles of the desired size.

The acetalization is catalyzed by the use of an organic or inorganic acid in an amount that will effectively allow protonation to occur, but will not significantly alter the final product by causing unwanted hydrolysis of the acetal groups.

20 Examples of suitable aldehydes useful in preparing the first cyclic acetal group of the acid-substituted ternary acetal polymers described herein include:

formaldehyde  
acetaldehyde  
propionaldehyde  
25 n-butyraldehyde  
isobutyraldehyde  
4-hydroxybutyraldehyde  
n-valeraldehyde  
5-hydroxyvaleraldehyde  
30 n-caproaldehyde  
n-heptaldehyde  
and the like.

Examples of suitable aldehydes useful in preparing the second cyclic acetal group of the acid-substituted ternary acetal polymers described herein include:

35 2-phenyl propionaldehyde  
3-phenyl butyraldehyde  
benzaldehyde  
2-hydroxy benzaldehyde  
4-hydroxy benzaldehyde  
40 2,4-dihydroxy benzaldehyde  
cinnamaldehyde  
hydrocinnamaldehyde  
biphenyl carboxaldehyde  
indole carboxaldehyde  
45 salicylaldehyde  
piperonal  
furfural  
and the like.

50 Examples of suitable aldehydes useful in preparing the third cyclic acetal group of the acid-substituted ternary acetal polymers described herein include:

2-formyl phenoxy acetic acid  
glyoxylic acid  
semisuccinaldehyde  
4-formyl phenoxy acetic acid  
55 2-carboxybenzaldehyde  
4-carboxybenzaldehyde  
2-formyl phenoxy sulfonic acid  
2-formyl phenoxy phosphonic acid

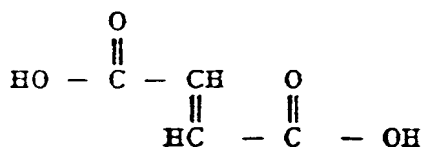
and the like.

An especially preferred acid-substituted ternary acetal polymer for use in this invention comprises about 3 mole % of vinyl alcohol moieties, about 12 mole % of vinyl acetate moieties, about 48 mole % of cyclic acetal moieties derived by reaction with propionaldehyde, about 12 mole % of cyclic acetal moieties derived by reaction with 3-phenyl butyraldehyde, and about 25 mole % of cyclic acetal moieties derived by reaction with 2-formyl phenoxy acetic acid.

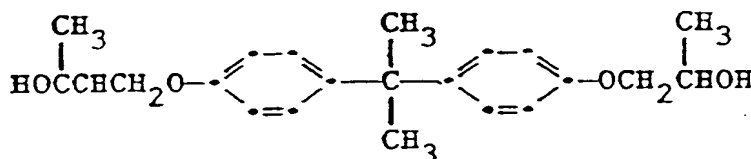
Another especially preferred acid-substituted ternary acetal polymer for use in this invention comprises about 7 mole % of vinyl alcohol moieties, about 12 mole % of vinyl acetate moieties, about 17 mole % of cyclic acetal moieties derived by reaction with n-butyraldehyde, about 34 mole % of cyclic acetal moieties derived by reaction with benzaldehyde and about 30 mole % of cyclic acetal moieties derived by reaction with glyoxylic acid.

Polyvinyl alcohols suitable for use as starting materials in preparing the acid-substituted ternary acetal polymers are well known commercially available materials. They preferably have an average molecular weight in the range of from about 3,000 to about 120,000. Examples of suitable polyvinyl alcohols include those available in a range of molecular weights from AIR PRODUCTS CORPORATION under the trademarks AIRVOL 203, AIRVOL 205, AIRVOL 523 and AIRVOL 540. Other suitable polyvinyl alcohols include those available from HOECHST-CELANESE under the trademarks MOWIOL 4-88, MOWIOL 5-88, MOWIOL 18-88, MOWIOL 26-88, and MOWIOL 40-88.

As indicated hereinabove, the radiation-sensitive compositions include an unsaturated polyester as well as an acid-substituted ternary acetal polymer. The unsaturated polyester employed is a copolyester of an unsaturated dicarboxylic acid such as fumaric acid or maleic acid, or mixtures thereof, and an oxyalkylene ether of an alkylidene diphenol. A typical example is the copolyester of fumaric acid which has the formula:



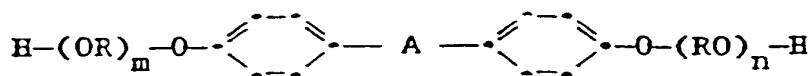
and polyoxypropylene-2,2'-bis(4-hydroxyphenyl)propane which has the formula:



Such copolyesters are well known in the art and are described, for example, in British Patents 722,264, 722,265, 722,266 and 722,273. They are available commercially from Reichhold Chemicals, Inc., as ATLAC 382E BISPHENOL FUMARATE RESIN (also known as ATLAC 32-629-00) and related resins ATLAC 382.05 (a solution of ATLAC 382E in styrene), ATLAC 32-631-000 (also known as ATLAC 382ES), ATLAC 32-628-00 (also known as ATLAC 382A) and ATLAC 32-630-00 (also known as ATLAC 382ESA); from CARGILL INC. as CARGILL 51-5184 resin and CARGILL 74-7451 resin; and from UNION CAMP CORPORATION as UNI-REZ 1042 resin.

To prepare the unsaturated polyester, an alkylene oxide, such as propylene oxide, is condensed with an alkylidene diphenol such as bisphenol-A, to give the bis-hydroxyalkyl derivative which, in turn, is reacted with an unsaturated acid, such as fumaric acid, to give the unsaturated polyester.

As described in British Patent No. 722,264, the suitable oxyalkylene ethers of an alkylidene diphenol can be generically represented by the formula:



wherein A is a 2-alkylidene radical of 3 or 4 carbon atoms, R is an alkylene radical of 2 or 3 carbon atoms, m and n are each at least one and the sum of m and n is not greater than 3. The esterifying dicarboxylic acid is predominantly fumaric acid, or maleic acid or mixtures thereof, but may include minor proportions of saturated aliphatic acids, aromatic acids or other unsaturated aliphatic acids, such as, for example, succinic acid, sebacic acid, phthalic acid or itaconic acid.

Copolyesters of an unsaturated carboxylic acid and an oxyalkylene ether of an alkylidene diphenol have been found to be especially useful in alleviating problems of blinding that can occur with lithographic printing plates containing an acid-substituted ternary acetal polymer. They provide enhanced properties in this regard without significantly detracting from other important characteristics of the composition. Certain other polymers evaluated were found to also alleviate the blinding problem to some extent but to introduce one or more undesirable features. Examples of such polymers are homoacetals, polyvinyl acetates, epoxies, acrylates and urethanes.

The unsaturated polyesters utilized herein have been employed heretofore in lithographic printing plates, for example, in the printing plates described in U.S. Patents 5,045,432, 5,053,315 and 5,061,600 but use thereof in combination with acid-substituted ternary acetal polymers is neither disclosed nor suggested in the prior art.

In addition to a diazo resin, the acid substituted ternary acetal polymer and the unsaturated polyester, the imaging layer of the lithographic printing plate can optionally contain a variety of other ingredients such as colorants, stabilizers, exposure indicators and surfactants. Particularly useful colorants are pigments, including phthalocyanine, anthraquinone and quinacridone pigments. The pigment selected should be one which contains a minimal amount of heavy metal and which forms a stable dispersion with the acid-substituted ternary acetal binder resin. Useful amounts of pigment are from about 1 to about 20 percent by weight of the photosensitive layer, more preferably from about 2 to about 12 percent by weight, and most preferably from about 4 to about 8 percent by weight. Effective stabilizers include both organic and inorganic acids, preferably citric, phosphoric, ascorbic or tartaric acids. Useful amounts of acid are from about 2 to about 6 percent by weight of the photosensitive layer, more preferably from about 2.5 to about 5 percent by weight, and most preferably from about 3 to about 4 percent by weight. Useful exposure indicators are dyes which are pH sensitive and which do not couple with diazonium compounds. Examples of such dyes include eosin, azobenzene, Victoria Blue, 4-phenylazo diphenylamine, methyl violet and phenolphthalein. Useful amounts of the dye are from about 0.01 to about 3 percent by weight of the photosensitive layer, more preferably from about 0.05 to about 2 percent by weight, and most preferably from about 0.1 to about 1 percent by weight. Useful surfactants include fluorocarbon surfactants, such as FC-430 surfactant from 3M Corporation or Zonyl NS surfactant from DuPont, and silicone surfactants such as Silwet L-7606 surfactant from Union Carbide Corporation or BYK surfactant from BYK CHEMIE. The surfactant is used in an amount of from about 0.1 to about 4 percent by weight of the photosensitive layer, more preferably from about 0.5 to about 2.5 percent by weight, and most preferably from about 1 to about 2 percent by weight.

In forming the photosensitive layer, the diazo resin, the acid-substituted ternary acetal polymer, the unsaturated polyester and the optional ingredients are dispersed in a suitable solvent or mixture of solvents. Particularly useful solvents include 2-methoxyethanol and the acetate thereof, 1-methoxy-2-propanol and the acetate thereof, 2-ethoxyethanol and the acetate thereof, toluene, diisobutyl ketone, butyrolactone, N-methyl pyrrolidone, methyl lactate, ethyl acetate, dimethyl formamide, tetrahydrofuran, methylethyl ketone and butyl acetate.

The support for the lithographic printing plate is typically formed of aluminum which has been grained, for example by electrochemical graining, and then anodized, for example, by means of anodizing techniques employing sulfuric acid and/or phosphoric acid. Methods of both graining and anodizing are very well known in the art and need not be further described herein.

The acid-substituted ternary acetal polymers and unsaturated polyesters described herein can be employed in dual layer lithographic printing plates in which a radiation-sensitive layer comprising a photocrosslinkable polymer is coated over a radiation-sensitive layer containing a diazo resin. Photocrosslinkable polymers which are particularly useful for this purpose are those containing the photosensitive group -CH=CH-CO- as an integral part of the polymer backbone, especially the p-phenylene diacrylate polyesters. These polymers are described, for example, in U. S. patents 3,030,208, 3,622,320, 3,702,765 and 3,929,489. A typical example of such a photocrosslinkable polymer is the polyester prepared from diethyl p-phenylenediacrylate and 1,4-bis( $\beta$ -hydroxyethoxy)cyclohexane, which is comprised of recurring units of the formula:



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Component	Weight %
Diazo resin <sup>(1)</sup>	1.111
H <sub>3</sub> PO <sub>4</sub> (85%)	0.106
Butyrolactone	13.545
1-Methoxy-2-propanol	69.346
4-Phenyl azodiphenylamine	0.017
Ternary acetal polymer <sup>(2)</sup>	0.705
Tetrahydrofuran	10.957
BYK 306 (10%) <sup>(3)</sup>	0.210
Unsaturated polyester <sup>(4)</sup>	0.470
Pigment dispersion <sup>(5)</sup>	3.533
	100.000

<sup>(1)</sup> Condensation product of 3-methoxy-4-diazo diphenyl amine sulfate and an isomeric mixture of methoxymethyl substituted diphenyl ethers isolated as the mesitylene sulfonate salt.

<sup>(2)</sup> Acid-substituted ternary acetal polymer comprising about 2 mole % of vinyl alcohol moieties, about 12 mole % of vinyl acetate moieties, about 48 mole % of cyclic acetal moieties derived by reaction with propionaldehyde, about 12 mole % of cyclic acetal moieties derived by reaction with 3-phenyl butyraldehyde, and about 25 mole % of cyclic acetal moieties derived by reaction with 2-formyl phenoxy acetic acid.

<sup>(3)</sup> A polyether modified dimethyl polysiloxane surfactant manufactured and sold by BYK CHEMIE.

<sup>(4)</sup> Copolyester of fumaric acid and polyoxypropylene-2,2'-bis(4-hydroxyphenyl)propane.

<sup>(5)</sup> The pigment dispersion was prepared by milling 5.3% Hostapern Blue B2G pigment, available from HOECHST-CELANESE Company, and the ternary acetal polymer described in (2) above in a solvent mixture of butyrolactone and 1-methoxy-2-propanol (15:85 w/w).

The printing plate was also developed with developing compositions within the scope of this invention as described hereinafter in Table I. Each of these developing compositions was the same as the control except that it additionally contained the ingredients referred to as "additives" in Table I.

The printing plate which was tested had been aged for three months at ambient conditions so that it would be more difficult to process than a fresh coating. The plate was given 162 units of exposure through a KODAK T-14 step wedge and hand processed on newsprint for 45 seconds. The following observations were made and recorded:

(1) cleanout time - the time in seconds required to remove the coating from all non-image areas

(2) solid step - the maximum density step of the T-14 image reproduced on the plate

(3) ghost step - the last visible step of the T-14 image reproduced on the plate.

In a KODAK model XL85 plate processor, the distance between the nips of the rollers at the entrance and the exit of the developer sections is 37 centimeters. The distance from the entrance roller nip to the first developing brush is 18 centimeters while the distance to the second brush is 28 centimeters. When the machine is run at the recommended throughput speed of 90 centimeters per minute, the times to the first brush, second brush, and exit of the developer section of the machine are 12 seconds, 18 seconds and 24 seconds, respectively. Therefore, it is absolutely essential for cleanout to occur in less than 24 seconds to assure a fully processed non-image area of the plate. It is desirable for the cleanout to occur in less than 18 seconds so that the mechanical action of the second brush can assist removal of the coating, and ideally, cleanout should occur in less than 12 seconds to fully utilize both brushes during the developing process.

The cleanout times reported in Table I for hand processing correspond well to the relative rate of processing in the machine, i.e., plates that require longer than 24 seconds to cleanout during hand processing will also be incompletely processed in the machine. Plates that cleanout by hand processing in less than 18 seconds are almost always completely clean in the non-image areas of the plate when processed in the machine.

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In a further test procedure, the ingredients referred to as "additives" in Table I were added to the control developer after 276 square meters of plate material had been processed in 19 liters of developer. This is the recommended life of the developer. After the additives had dissolved in the "used" polymer-laden developer, eight drops were applied to an ungrained phosphoric acid anodized plate support, the solution was dried at 50 °C for 18 hours, and then immersed in a tray of fresh control developer. The tray was rocked gently for eight minutes and the ease or difficulty of removal of the dried spotted material was observed. The time for removal of the spot and the amount of residue were recorded. Obviously, samples with spots that were removed quickly with only a slight residue or no residue were most beneficial. This would simulate the ability of the developer to redissolve materials that had deposited on the interior surfaces, brushes (or plushes), or rollers in the machine.

The developing compositions evaluated are described in Table I below. In some of the developing compositions, 2-phenoxyethanol is utilized as an additive since the combination of 2-phenoxyethanol and 2-phenoxypropanol gives a more active developer than the control developer which contains only 2-phenoxypropanol.

Table I

	<u>Example No.</u>	<u>Additives</u>	<u>Weight %</u>
5	Control	--	--
	1	TIRON*	1.0
		CARBOWAX 200	1.0
		Trisodium citrate dihydrate	0.5
10	2	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 200	1.0
		Trisodium citrate dihydrate	0.5
15	3	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 350	1.0
		Trisodium citrate dihydrate	0.5
20	4	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 600	1.0
		Trisodium citrate dihydrate	0.5
25	5	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 200	1.0
		Trisodium citrate dihydrate	0.5
		Di-n-octylamine	0.7
30	6	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 200	0.5
		Trisodium citrate dihydrate	0.4
		Di-n-octylamine	0.8
35	7	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 350	1.0
		Trisodium citrate dihydrate	0.5
40		Di-n-octylamine	0.7
	8	TIRON	1.0
		2-Phenoxyethanol	1.0
		CARBOWAX 600	1.0
45		Trisodium citrate dihydrate	0.5
		Di-n-octylamine	0.7
	9	TIRON	1.0
		3-Hydroxy-2-naphthoic acid	0.2
50		2-Phenoxyethanol	1.0
		CARBOWAX 200	1.0
		Trisodium citrate dihydrate	0.5

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<u>Example No.</u>	<u>Additives</u>	<u>Weight %</u>
10	TIRON	1.0
	2,4-Dihydroxy-benzoic acid	0.2
	2-Phenoxyethanol	1.0
	CARBOWAX 600	1.0
	Trisodium citrate dihydrate	0.5
	Di-n-octylamine	0.7

\*TIRON is a trademark for 4,5-dihydroxy-1,3-benzene-disulfonic acid disodium salt which is available commercially from ALDRICH CHEMICALS

The results obtained from the evaluation of the developing compositions described in Table I are summarized in Table II below.

Table II

Example No.	Spot Test		Cleanout Time (seconds)	Speed Solid/Ghost
	Time (minutes)	Residue		
Control	8	Heavy	21	3/9
1	1	Clean	16	3+/10
2	1	Clean	11	3+/10
3	2	Clean	10	3+/10
4	4	Clean	10	3/9
5	2	Slight	15	3+/10
6	1.5	Clean	12	3+/10
7	1	Clean	10	3/10
8	1	Clean	12	3/10
9	4	Clean	20	3+/11
10	1	Clean	13	3/10

As shown by the data in Table II, developing compositions within the scope of this invention provide superior results in comparison with the control developer in regard to both cleanout rate (cleanout times of as low as 10 seconds as compared with 21 seconds for the control) and spot removal (times as low as 1 minute as compared with 8 minutes for the control).

While applicants do not wish to be bound by any theoretical explanation of the manner in which their invention functions and the exact mechanisms are not clearly understood, it is postulated that the hydroxylated aromatic acid salts could complex with the diazo resin through the hydroxyl functional group while the acid functional group could provide solubilization in aqueous alkaline developer. It might also be the case that the aromatic character of the hydroxylated aromatic acid salt could space tightly packed linear aliphatic chains of dry developer, thus allowing the developer to more easily penetrate the dry polymer matrix and loosen and remove the deposit. The (polyalkylene glycol) and alkali metal citrate could assist in the performance of the developing composition by retarding water evaporation.

## Claims

1. An aqueous alkaline developing composition that is useful in developing negative-working lithographic printing plates, said composition comprising:

- (1) an organic solvent,
- (2) an anionic surface active agent,
- (3) an alkali metal tetraborate,
- (4) an alkali metal salt of an aliphatic monocarboxylic acid,



- (5) an alkali metal salt of an aliphatic dicarboxylic acid,
- (6) an alkali metal citrate,
- (7) a poly(alkylene glycol),
- (8) an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid, and
- (9) an alkaline buffering system in an amount sufficient to provide an alkaline pH.

2. A developing composition as claimed in claim 1 wherein said organic solvent is present in an amount of from 2.5 to 7 weight percent, said anionic surface active agent is present in an amount of from 1.2 to 8 weight percent, said alkali metal tetraborate is present in an amount of from 0.1 to 3 weight percent, said alkali metal salt of an aliphatic monocarboxylic acid is present in an amount of from 2.5 to 8 weight percent, said alkali metal salt of an aliphatic dicarboxylic acid is present in an amount of from 0.4 to 3 weight percent, said alkali metal citrate is present in an amount of from 0.4 to 2 weight percent, said poly(alkylene glycol) is present in an amount of from 0.4 to 2 weight percent, and said alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid is present in an amount of from 0.4 to 2 weight percent.
3. A developing composition as claimed in claim 1 or claim 2 wherein the pH is in the range of from 8 to 12.
4. A developing composition as claimed in claim 1 or claim 2 wherein the pH is in the range of from 9 to 10.
5. A developing composition as claimed in any of claims 1 to 4, wherein said alkali metal salt of an aliphatic monocarboxylic acid is a salt of octanoic acid, nonanoic acid, decanoic acid or dodecanoic acid.
6. A developing composition as claimed in any of claims 1 to 5, wherein said alkali metal salt of an aliphatic dicarboxylic acid is a salt of sebacic acid, suberic acid or succinic acid.
7. A developing composition as claimed in any of claims 1 to 6, wherein said alkali metal citrate is trisodium citrate.
8. A developing composition as claimed in any of claims 1 to 7, wherein said alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid is the sodium salt of 3-hydroxy-2-naphthoic acid or the disodium, salt of 4,5-dihydroxy-1,3-benzenedisulfonic acid.
9. A developing composition as claimed in any of claims 1 to 8, wherein said alkaline buffering system comprises potassium hydroxide and potassium carbonate.
10. A developing composition as claimed in any of claims 1 to 9, wherein said composition additionally comprises a long chain aliphatic amine.

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**14.12.94 Bulletin 94/50**(71) Applicant: **EASTMAN KODAK COMPANY**  
**343 State Street**  
**Rochester New York 14650-2201 (US)**(72) Inventor: **Miller, Gary Roger, c/o Eastman**  
**Kodak Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201 (US)**  
Inventor: **Walls, John E., c/o Eastman Kodak**  
**Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201 (US)**  
Inventor: **Felker, Melanie Ann, c/o Eastman**  
**Kodak Company**  
**Patent Department,**  
**343 State Street**  
**Rochester, New York 14650-2201 (US)**(74) Representative: **Nunney, Ronald Frederick**  
**Adolphe et al**  
**Kodak Limited**  
**Patent Department**  
**Headstone Drive**  
**Harrow Middlesex HA1 4TY (GB)**(54) **Aqueous developer for lithographic printing plates which exhibits reduced sludge formation.**

(57) Aqueous alkaline developing compositions useful in the development of negative-working lithographic printing plates are comprised of an organic solvent, an anionic surface active agent, an alkali metal tetraborate, an alkali metal salt of an aliphatic monocarboxylic acid, an alkali metal salt of an aliphatic dicarboxylic acid, an alkali metal citrate, a poly-(alkylene glycol), an alkali metal salt of an hydroxylated aromatic carboxylic or sulfonic acid and sufficient alkaline buffering system to provide an alkaline pH. The developing composition is resistant to oxidation, highly effective in dissolution-type processing, able to effectively desensitize the background areas of the printing plate, and capable of preventing excessive deposits in a processing machine and

rapidly redissolving deposits that do form.

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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 20 3487

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X,Y	EP-A-0 134 407 (AMERICAN HOECHST CORPORATION) 20 March 1985 * page 8, line 1 - page 9, column 7; claim 1 * ---	1-4	G03F7/32
Y	EP-A-0 413 559 (HOECHST CELANESE CORPORATION) 20 February 1991 * examples 1-5 * ---	1-10	
Y	GB-A-2 183 858 (AMERICAN HOECHST CORPORATION) 10 June 1987 * page 8; example 4 * ---	1-10	
E	EP-A-0 580 532 (EASTMAN KODAK COMPANY) 26 January 1994 * claim 1 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03F
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
MUNICH		16 September 1994	Thiele, N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

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